CARBON FIBER, METHOD FOR PRODUCING THE SAME AND APPARATUS THEREFOR

CROSS REFERENCE TO RELATED APPLICATIONS

This application is an application filed under 35 U.S.C. §111(a) claiming benefit pursuant to 35 U.S.C. §119(e)(1) of the filing date of Provisional Application 60/245,715 filed November 6, 2000 pursuant to 35 U.S.C. §111(b).

FIELD OF THE INVENTION

The present invention relates to a carbon fiber which has been produced through a thermal decomposition reaction from a raw material predominantly containing a carbon source and a transition metal serving as a catalyst. The present invention also relates to a method for producing the carbon fiber; to a high-temperature heat treatment method for the carbon fiber; and to a heat treatment apparatus for the method.

BACKGROUND OF THE INVENTION

A variety of processes for producing fine carbon fiber are known. A process in which an organic compound, such as benzene, serving as a raw material, and an organic transition metal compound ,such as ferrocene, serving as a metallic catalyst, are introduced into a high-temperature reaction furnace together with a carrier gas to produce fine carbon fiber on a substrate is disclosed in Japanese Patent Application Laid-Open (*kokai*) No. 60-27700. A process in which fine carbon fiber is produced in a dispersed state is disclosed in Japanese Patent Application Laid-Open (*kokai*) No. 60-54998; and a process in which fine carbon fiber is grown on a reaction furnace wall is disclosed in Japanese Patent No. 2778434. The carbon fiber produced through such processes are called "vapor grown carbon fiber," and are widely used in industry.

Through the aforementioned processes, fibrous fine carbon fiber having a diameter of about 0.005-5 μm and a length of about 1-1,000 μm can be produced. Immediately after production, the carbon fiber has a very low bulk density and is fluffy. Therefore, the carbon fiber is usually subjected to pressing to increase its bulk density, thereby facilitating treatment of the resultant carbon fiber in the subsequent step.

However, the residue of a non-reacted catalyst, a non-fibrous carbide, and

tar are contained between filaments of the "as produced" carbon fiber (i.e., crude carbon fiber). Therefore, in the subsequent step crude carbon fiber is subjected to treatment by means of various techniques in order to remove a non-fibrous substance. In particular, organic transition metal compounds used as catalysts for producing the carbon fiber remain in the crude carbon fiber filaments in amounts of several mass% when reduced to the metals, and the presence of the metals is not preferred from the viewpoint of characteristics of the carbon fiber during use.

Heat treatment of carbon fiber is usually carried out in order to remove a non-reacted organic substance or to regulate properties and characteristics of the carbon fiber. In accordance with use of the carbon fiber, the carbon fiber is subjected to heat treatment in order to remove tar deposited onto the fiber or to carry out crystal regulation or crystal growth in relation to carbon layers (carbon sheets). For example, the carbon fiber is subjected to heat treatment in an inert gas at a temperature within a range of 900-2,000°C to carbonize tar deposited onto the surface of the fiber and simultaneously vaporize a certain amount of the tar. Alternatively, the carbon fiber is subjected to high-temperature heat treatment at 2,000-3,300°C to graphitize the fiber for crystal regulation or crystal growth in relation to carbon layers. During such heat treatment, an impurity contained in the carbon fiber, such as a transition metal used as a catalyst for the reaction, is vaporized and removed from the fiber.

From the viewpoint of production efficiency, production of carbon fiber through the aforementioned process, pressing of the fiber, and heat treatment of the fiber are usually carried out in an apparatus that includes continuous production lines. Experimentally, such procedures are carried out in a batch-type furnace.

In the aforementioned apparatus for heat treatment, carbon fiber is heated at a temperature as high as 2,000-3,300°C. Therefore, in consideration of thermal and chemical stability of a material of the apparatus at such a high temperature, a hollow cylinder formed from graphite or carbon is used as a heating body for a heat treatment furnace. Alternatively, a heating body in which a heating belt is placed around a hollow cylindrical body is used. Usually, a heat insulator formed from carbon fiber or micropowder of carbon black or coke is placed around such a heating body.

In order to continuously graphitize carbon fiber efficiently by use of a high-temperature heat treatment furnace, as described in Japanese Patent No. 2744617 and Japanese Patent Application Laid-Open (*kokai*) No. 8-60444, carbon fiber to be heated is continuously fed into the furnace through one end thereof, an inert gas serving as a carrier gas is passed through the furnace in a direction opposite to the feeding direction of the carbon fiber, the carbon fiber is heated at a high temperature in the furnace, and the resultant carbon fiber is continuously discharged through the other end of the furnace and then cooled. When a small amount of carbon fiber is to be subjected to heat treatment, a batch-type furnace shown in Fig. 1 is usually employed, in which the carbon fiber 6 is fed into the furnace 3 through one end thereof, which is provided with an opening and closing shutter 9, and the heat-treated carbon fiber is discharged through the same end.

When a large amount of carbon fiber is to be subjected to heat treatment continuously, a furnace shown in Fig. 2 is employed, in which the carbon fiber is fed into the furnace through one end thereof, which is provided with an opening and closing shutter 9, and discharged through the other end, which is provided with an opening and closing shutter 10.

The entire atmosphere within such a furnace must be non-oxidative, and thus, usually, an inert gas is passed throughout the furnace by feeding the gas through one end of a substance to be heated and discharging the gas through the other end. In the case of the furnace shown in Fig. 1, an inert gas is fed through an inlet 4 provided on the back side of the furnace, and the gas is discharged through an outlet 5 provided near an end of the furnace through which carbon fiber is fed and discharged. In the case of the furnace shown in Fig. 2, an inert gas is fed through an inlet 4 provided near an end of the furnace through which carbon fiber is discharged, and the gas is discharged through an outlet 5 provided near an end of the furnace through which the carbon fiber is fed.

Crude carbon fiber that is to be heated has a low bulk density and is inconvenient to convey. Therefore, when the carbon fiber is fed into a heating furnace, the carbon fiber is placed in a container, such as a graphite crucible, or subjected to pressing as described above.

In a high-temperature heat treatment furnace, the temperature of an inlet portion for feeding a substance to be heated or that of an outlet portion for

discharging the substance is low, and the temperature is highest in the center portion. In a continuous heat treatment furnace having two open ends, temperature is highest at a substantially intermediate portion between either end and the center of the furnace. Similarly, in a furnace in which a substance to be heated is fed or discharged through one end, the temperature is highest at a substantially intermediate portion between the end and the center of the furnace.

An impurity contained in carbon fiber, such as a transition metal used as a catalyst for reaction, is temporarily vaporized at a high-temperature section in the vicinity of the center of a high-temperature heat treatment furnace, accompanied by an inert gas fed through one end of the furnace, and transferred to the other end of the furnace. Since the temperature of the atmosphere is low at the other end, the vaporized impurity (e.g., the vaporized transition metal) is condensed to solidify. The resultant transition metal is easily reacted with a material which constitutes a heating body or a heat insulator, such as graphite or carbon to form a carbide of transition metal. The thus-formed carbide may cause generation of holes in the heating body and impairment of the heating body or the heat insulator.

A transition metal element, such as Fe, Ni, Co, or Mo, may be used in a raw material of an organic compound serving as a catalyst, and such a transition metal is condensed to solidify at a temperature of about 2,000°C or lower.

Since the heat insulator has a large specific surface area, the insulator easily reacts with a transition metal, and a carbide is formed; i.e., a certain amount of the insulator is consumed for the formation of the carbide. As a result, the insulator can no longer be used.

In view of the foregoing, an object of the present invention is to provide a method for preventing impairment of or damage to a furnace, which is mainly attributable to a transition metal contained in carbon fiber; and a method and apparatus for obtaining carbon fiber through heat treatment in a furnace. The carbon fiber is not susceptible to impurities.

SUMMARY OF THE INVENTION

The present invention provides the following embodiments:

(1) a high-temperature heat treatment method for carbon fiber which has been produced through thermal decomposition reaction of a carbon source and a transition metal catalyst, serving as main raw materials, which method is

comprises vaporizing an impurity, such as a transition metal, contained in the carbon fiber, and discharging the impurity through a high-temperature section of a heat treatment furnace while being accompanied by a carrier gas;

(2) a high-temperature heat treatment method for carbon fiber according to (1), further comprising cooling the impurity accompanied by the carrier gas to solidify the impurity, and recovering the impurity;

(3) a high-temperature heat treatment method for carbon fiber according to (1) or (2), further comprising returning the carrier gas to the heat treatment furnace, after the impurity is recovered, and recycling the gas to be passed through the furnace;

(4) a high-temperature heat treatment method for carbon fiber according to any one of (1) to (3), wherein the amount of any of Fe, Ni, and Co contained in the carbon fiber which has undergone heat treatment is about 100 mass ppm or less;

(5) a high-temperature heat treatment apparatus for heat-treating carbon fiber which has been produced through thermal decomposition reaction of a carbon source and a transition metal catalyst, serving as main raw materials, which furnace comprises a hollow cylindrical heating furnace body formed from graphite or carbon having at least an open end or an end which can be opened or closed; a heat insulator provided around the hollow cylindrical furnace body; a feed inlet for feeding a carrier gas into the furnace provided in the vicinity of a feed end and/or discharge end, and a discharge outlet for discharging the carrier gas to the outside of the furnace is provided in the vicinity of a highest-temperature section of the furnace, wherein the carbon fiber to be heated is continuously fed, heated, and discharged through the furnace;

(6) a high-temperature heat treatment apparatus according to (5), wherein heat treatment can be carried out at approximately 2,000-3,000°C;

(7) a high-temperature heat treatment apparatus according to (5) or (6), further comprising a recovery site for cooling an impurity contained in a carrier gas to solidify provided adjacent to the carrier gas discharge outlet of the furnace;

(8) a high-temperature heat treatment apparatus according to (7), which furnace further comprises a mechanism for returning the carrier gas to the carrier gas feed inlet after recovery of the impurity;

(9) a method for producing the carbon fiber, comprising a step of a thermal decomposition reaction of a carbon source and a transition metal catalyst, serving as main raw materials, and a step of a heat treating the thermal decomposition, wherein said step of heat treating comprises the high-temperature heat treatment method for carbon fiber according to any one of (1) to (4);

(10) a carbon fiber obtainable by the high-temperature heat treatment method for carbon fiber according to any one of (1) to (3);

(11) a carbon fiber obtainable by the method for producing the carbon fiber according to (9); and

(12) the carbon fiber according to (10) or (11), comprising about 100 mass ppm or less of a metal element selected from the group consisting of Fe, Ni, Co, Cu, Mo, Ti, V and Pd.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a cross-sectional view of a furnace body and peripheral apparatus employed in a conventional batch-type heat treatment method.

Fig. 2 is a cross-sectional view of a furnace body and peripheral apparatus employed in a conventional continuous heat treatment method.

Fig. 3 is a cross-sectional view of a furnace body and peripheral apparatus employed in the batch-type heat treatment method according to the present invention.

Fig. 4 is a cross-sectional view of a continuous heat treatment furnace according to the present invention.

DESCRIPTION OF THE PRESENT INVENTION

The present invention provides carbon fiber, a method for producing the carbon fiber and apparatus for the carbon fiber. In the method of the present invention, carbon fiber that is to be heated is continuously passed through a high-temperature heat treatment apparatus (a high-temperature heat treatment furnace) and subjected to high-temperature heat treatment for removal of an impurity while an inert gas is passed through the furnace. The furnace includes a hollow cylindrical heating furnace body formed from graphite or carbon and a heat insulator provided around the furnace body. The inert gas is discharged

from the heat treatment furnace without causing the impurity, such as a catalyst metal contained in the gas, to solidify by condensation or to react with the furnace material, which would adversely affect the furnace.

Furthermore, the present invention provides a method and a mechanism for recovering the impurity through solidification from the inert gas discharged from the high-temperature heat treatment furnace, and returning the resultant inert gas to the furnace.

In the high-temperature heat treatment apparatus used in the present invention, heating can be carried out at a temperature of at least about 2,000°C or at a temperature as high as about 3,000°C or higher, and is preferably carried out at about 3,300°C. Such an apparatus usually includes a vertical or horizontal hollow cylindrical heating furnace body. Usually, a substance to be heated is fed through one end of the furnace body, heated in the furnace body, and discharged through the same end or the other end.

Since the cylindrical furnace body is used at a high temperature, the furnace body is formed from a material, such as graphite or carbon. In consideration of durability, the furnace body is preferably used as a cylindrical heating body. In order to heat the cylindrical furnace body, several techniques can be employed, including a Tammann technique in which a high current is applied directly to the furnace body, a high-frequency induction technique in which an induced current is generated by use of an induction coil, and a technique in which the furnace body is heated by use of a heating body, such as a carbon belt, placed around the furnace body.

The cylindrical furnace body is covered with a carbon fiber heat insulator in order to maintain the temperature of the furnace body and to protect the body from any damage. Usually, a heat treatment furnace includes such a cylindrical furnace body and a heat insulator.

The heat treatment method of the present invention will next be described in detail.

When a substance to be heated (i.e., carbon fiber) is subjected to high-temperature heat treatment, a furnace is impaired through oxidation when carbon fiber is not heated in a non-oxidative atmosphere. In the present invention, since the hollow cylindrical heating furnace body is formed from carbon, the furnace body must be protected from oxidation. Therefore, an inert

gas serving as a carrier gas must be passed through the furnace. Examples of the inert gas include N_2, helium, argon, xenon, and krypton, and these may be used alone or in combination. Preferably, N_2 or argon is used, since they are readily available.

The relation between gas circulation, furnace temperature, and impurities in a conventional furnace will be described by taking a batch-type furnace shown in Fig. 1, as an example, in which a substance to be heated is fed through one end of the furnace. Fig. 1 shows a high-frequency induction-type furnace.

Usually, an inert gas is fed through a carrier gas inlet 4 provided at one end of a hollow cylindrical furnace body 3 in which a substance to be heated 6 is placed, and the inert gas is discharged through an outlet 5 provided at the other end of the furnace body, so that the inert gas does not stagnate in the furnace body and is passed throughout the furnace body.

A transition metal element, such as Fe, Ni, Co, or Mo, contained as an impurity in carbon fiber filaments is an element, which is derived from an organic compound of a transition metal used as a catalyst for producing carbon fiber, and thus such an element is not easily vaporized at about 2,000°C or lower. Therefore, the carbon fiber must be heated to about 2,000°C or higher, preferably to about 3,000°C.

The temperature in the vicinity of the carrier gas inlet 4 is slightly lower compared to other sections of the furnace body, since the inlet 4 is located near a furnace heat insulator 1. Therefore, in order to maintain the temperature of the substance 6 at a temperature at which the aforementioned metal can be vaporized, the substance 6 must be placed in a position at a distance from the back side of the furnace body. The length of the furnace body and the amount of the substance to be heated must be appropriately balanced.

A metal impurity vaporized from the substance 6 which has undergone high-temperature heat treatment is accompanied by an inert gas serving as a carrier gas, and transferred to the carrier gas outlet 5. When the gas reaches the vicinity of the outlet 5, the temperature of the gas decreases, since the outlet is distant from a heating zone. Also, the temperature of the gas decreases in the vicinity of a position at which the hollow cylindrical furnace body 3 and the heat insulator 1 are connected. Therefore, the metal contained in the inert gas is condensed to solidify again. The metal is deposited onto the heat insulator 1 or

in the vicinity of the carrier gas outlet 5, or reacted with the furnace material, thereby causing corrosion.

Fig. 2 shows a conventionally used continuous heat treatment furnace in which a substance to be heated is fed through one end of the furnace and discharged through the other end. In this furnace, in a manner similar to that of the furnace shown in Fig. 1, a metal contained in an inert gas is easily condensed to solidify in the vicinity of a carrier gas outlet 5.

In the heat treatment furnace of the present invention, as shown in Fig. 3, an inert gas is preferably fed through an inlet 14 provided near an end, which is provided with an opening and closing shutter 19, through which a substance 16 to be heated is fed and through an inlet 14 provided at the back side of the furnace. Specifically, an inert gas is fed through the inlets provided near both ends of the furnace at which the temperature is low.

As described above, in the furnace, the inert gas contains an impurity such as a transition metal vaporized from carbon fiber. Therefore, the inert gas must be discharged to the outside of the furnace while the temperature of the gas is maintained as high as possible. An important feature of the present invention is that the inert gas is discharged from the vicinity of a highest-temperature section of the furnace.

Usually, a Tammann-type or high-frequency induction-type hollow cylindrical furnace 13 used in the present invention has a highest-temperature section in the vicinity of its center portion (i.e., the portion farthest from the two ends of the furnace), and thus the inert gas is discharged from the center portion.

Consequently, the inert gas can be discharged to the outside of the furnace without causing condensation and solidification of an impurity contained in the inert gas in the vicinity of a furnace heat insulator 11 or at a carrier gas outlet 15.

The thus-discharged gas may be cooled outside the furnace to solidify and to recover the impurity in, for example, a container. After the impurity is recovered, the resultant gas may be recycled as an inert gas by returning the gas to a line connected to the furnace.

According to the method of the present invention, the amount of an element impurity, such as Fe, Ni, Co, Cu, Mo, Ti, V, or Pd, preferably Fe, Ni, or Co, contained in a substance to be heated; i.e., carbon fiber produced through a thermal decomposition reaction from a carbon source and a catalyst metal,

serving as main raw materials, can be reduced to about 100 mass ppm or less.

The percentage removal of such a metallic element impurity increases by increasing the time for heat treatment of the substance in a furnace and the flow rate of a carrier gas. Therefore, such parameters (i.e., heat treatment time and carrier gas flow rate) may be determined in accordance with required impurity standards for carbon fiber.

A continuous furnace and an apparatus according to the method of the present invention will next be described with reference to a drawing. Fig. 4 shows a cross-sectional view of an apparatus including a high-frequency induction-type furnace body according to the present invention.

An artificial-graphite-made hollow cylindrical furnace body 23 which is to be heated has left and right open ends. The left end shown in Fig. 4 is connected through a tube, which is separately provided, to a line for a step prior to the heat treatment (a step of a thermal decomposition reaction etc.) so that it is closed. The right end is connected to a cooling chamber 32 through a tube, which is separately provided, and an opening and closing shutter 29.

A substance to be heated 26 (carbon fiber in the present invention), which has been produced in the prior step, is subjected to pressing or placed in a graphite crucible, and fed into the furnace body 23 through the left end by means of a driving apparatus. The hollow cylindrical furnace body 23 is heated through induction heating by use of an induction coil 22. The induction coil is covered with a heat insulator 21. A furnace 31 includes the induction coil 22 and the heat insulator 21.

Since the left and right ends of the hollow cylindrical furnace body 23 are open, the temperature of the furnace body is highest at its center portion. Heat treatment is carried out in a non-oxidative atmosphere, and thus an inert gas is introduced into the furnace body through carrier gas inlets 24 provided in the vicinity of the left and right open ends. The introduced inert gas is circulated through the furnace body, and then discharged through a carrier gas outlet 25 provided at a highest-temperature section of the center of the furnace body, to the outside of the furnace body by use of a gas suction pump 27.

The inert gas is discharged through the gas outlet 25 while the temperature of the gas is maintained at a high level. However, when the inert gas reaches an impurity solidification-recovery container 28, the temperature of the

inert gas decreases, and an impurity contained in the gas is solidified, the impurity predominantly containing a transition metal.

If necessary, a recovery container formed from, for example, graphite, carbon, or ceramic, may be provided at the site of the impurity solidification-recovery container 28. In addition, the recovery container may be filled with, for example, carbon fiber, carbon black, or carbon micropowder, to cause such material to react with the impurity.

After the impurity is recovered, the resultant gas may be returned to the furnace body through the carrier gas inlet 24 by means of a mechanism such as a pump. As shown in Fig. 4, the resultant gas is recycled by returning the gas to the furnace body through the gas inlet 24 provided in the vicinity of the end of the furnace body through which a substance to be heated is fed.

EXAMPLES

The present invention will be explained in more detail with reference to the Examples, which should not be construed as limiting the present invention. Unless otherwise indicated herein, all parts, percents, ratios and the like are by weight.

Heat treatment of carbon fiber was carried out by use of the aforementioned furnace in Fig. 4. The results will be described below.

Example 1:

Vapor grown carbon fiber (about 1000 kg) having a mean diameter of 0.2 μm and containing an element of iron(Fe) (i.e., impurity) in an amount of 2 mass% was subjected to continuous high-temperature heat treatment at 2,800°C in a hollow cylindrical furnace body having an inner diameter of about 15 cm, while argon gas was passed through the apparatus.

During heat treatment, the inert gas containing the impurity was temporarily discharged from a furnace body, the impurity was removed from the gas by use of an impurity solidification-recovery container filled with carbon micropowder, and the resultant gas was returned to the furnace.

After heat treatment of the carbon fiber (about 1000 kg) was completed, the furnace was subjected to inspection. Deposition of iron-containing carbide (about 0.1 kg) in a hollow cylindrical furnace body was observed, but no hole was found in the furnace body. Iron-containing carbide (about 20 kg) was recovered in the solidification-recovery container. Corrosion of a furnace heat insulator was

not observed, and no hole was found at an end of the furnace body through which the carbon fiber had been fed. The furnace body and the heat insulator were able to be reused.

The amount of Fe detected in the heat-treated carbon fiber was 30 mass ppm.

Example 2:

Vapor grown carbon fiber (about 500 kg) having a mean diameter of 0.02 μm and containing an element of iron in an amount of 3 mass% was subjected to continuous high-temperature heat treatment in a manner similar to Example 1.

After heat treatment of the carbon fiber (about 500 kg) was completed, the furnace was subjected to inspection. Deposition of iron carbide (about 0.1 kg) in a hollow cylindrical furnace body was observed, but no hole was found in the furnace body. Iron carbide (about 19 kg) was recovered in an impurity solidification-recovery container.

The amount of Fe detected in the heat-treated carbon fiber was 30 mass ppm.

Comparative Example:

Carbon fiber similar to that used in the Examples; i.e., vapor grown carbon fiber having a mean diameter of 0.2 μm and containing an element of iron(Fe) (i.e., impurity) in an amount of 2 mass%, was used. A conventional furnace which was heated through high-frequency induction heating shown in Fig. 2 was used. The furnace included an artificial graphite-made hollow cylindrical furnace body 3 having an inner diameter of about 15 cm. Argon gas was introduced through an inlet 4 provided near one end of the furnace body, and discharged by means of suction through an outlet 5 provided near the other end.

The carbon fiber (about 1000 kg) was subjected to continuous high-temperature heat treatment at 2,800°C. After heat treatment was completed, the artificial-graphite-made furnace body and a heat insulator 1 formed from carbon fiber were subjected to inspection. At an end through which the carbon fiber had been fed, deposition of iron carbide (about 2 kg) in the furnace body was observed and a hole was found in the furnace body. A cavity having a width of about 120mm, a length of about 400mm, and a depth of about 70mm was formed in the heat insulator provided around the furnace body, and iron-containing carbide ingot (about 7 kg) was deposited onto the cavity. Furthermore, a large

amount of iron carbide particles having a size of approximately 1-3 mm were deposited onto the heat insulator, and the entire heat insulator was impaired.

Changing of the hollow cylindrical furnace body and the heat insulator was necessary for carrying out the next run of heat treatment.

The amount of Fe detected in the heat-treated carbon fiber was 200 mass ppm.

According to the method for producing a carbon fiber of the present invention, even when carbon fiber, for example, vapor grown carbon fiber, is subjected to high-temperature heat treatment, impairment of a furnace body and a heat insulator, which is caused by solidification of an impurity contained in the carbon fiber or reaction between the impurity with carbon, can be prevented. When the apparatus of the present invention is used, the service life of the furnace body and the heat insulator can be prolonged. Furthermore, the frequency of inspection can be reduced, thus enhancing productivity. As a result, production costs can be greatly reduced.

In addition, the amount of a transition metal, such as Fe, Ni, Co, Cu, Mo, Ti, V, or Pd, preferably Fe, Ni, or Co, contained in the heat-treated carbon fiber can be reduced to about 100 mass ppm or less.

While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.